LA-UR-21-24934
Approved for public release; distribution is unlimited.

Title: Laboratory Investigation of Gas Transport Through Variably Saturated Rock

Author(s): Neil, Chelsea Wren
Boukhalfa, Hakim
Brug, William Patrick
Stauffer, Philip H.
Ortiz, John Philip
Xu, Guangping
Broome, Scott
Paul, Matthew
Greathouse, Jeffrey

Intended for: Presentation for Independent Review of LYNM Containment

Issued: 2021-05-21

Low Yield Nuclear Monitoring

Laboratory Investigation of Gas Transport Through Variably Saturated Rock

LANL: (EES-14) Chelsea Neil, Hakim Boukhalfa & Pat Brug

(EES-16) Phil Stauffer & John Ortiz

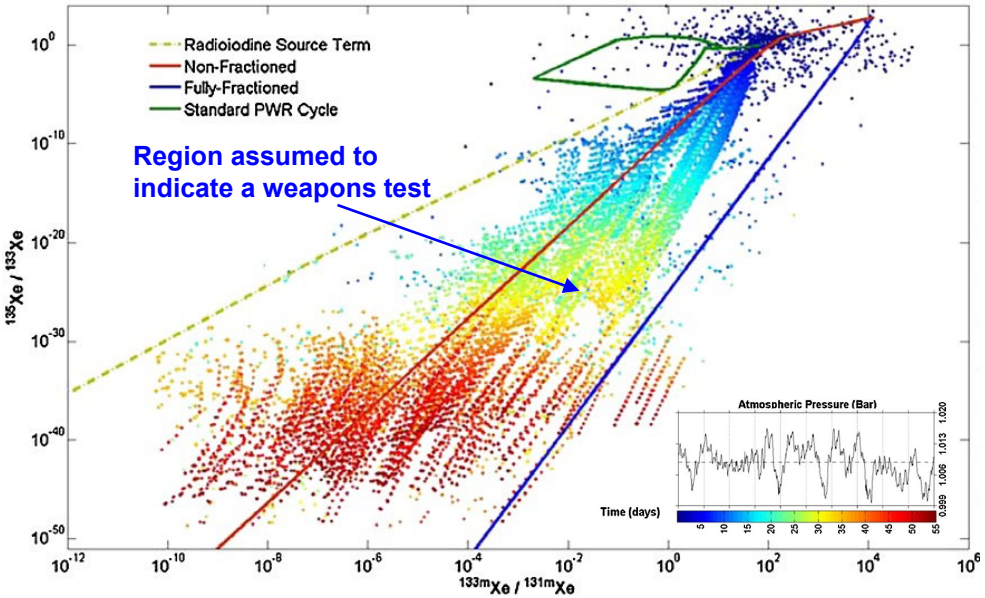
SNL: Guangping Xu, Scott Broome, Matt Paul & Jeffrey Greathouse

May 26, 2021

Los Alamos NATIONAL LABORATORY EST. 1943 | Lawrence Livermore National Laboratory | Pacific Northwest NATIONAL LABORATORY | Sandia National Laboratories | NNSA National Nuclear Security Administration

Project Overview

- Noble gas fission products, such as xenon (Xe), are monitored to detect nuclear tests
- For well-contained subsurface tests, transport to the surface will impact detected isotopic ratios, complicating event identification
- Role of water saturation in subsurface transport is not well understood
  - Historic tests have taken place near or below the water table



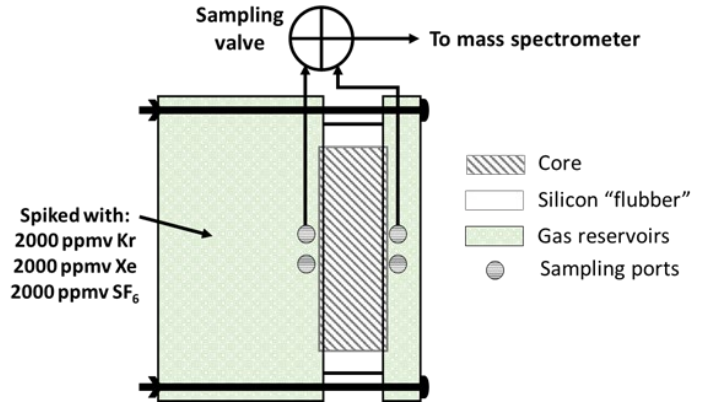
From Lowrey et al. *Geophysical Research Letters*, 40(1), (2013)

To accurately predict breakthrough times and fractionation, gas transport must be characterized through intact rock with variable saturation.

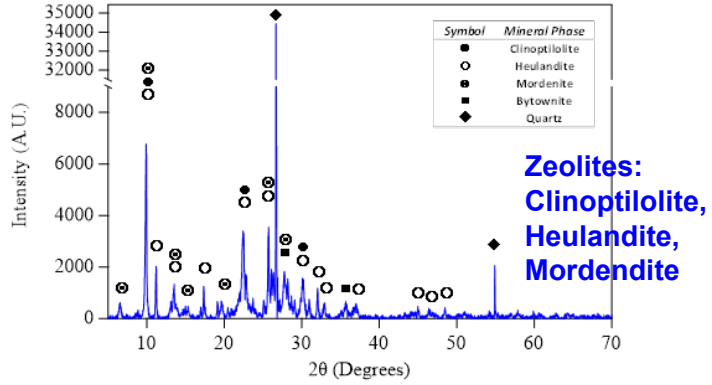
Technical Approach

- Rock core taken from the Nevada National Security Site
  - Zeolitic Nonwelded lithology at depth of 1445.7-1446.3 ft
- Core placed in diffusion cell
  - Larger reservoir spiked with gas mixture (krypton and xenon noble gases + sulfur hexafluoride, a commonly used tracer)
- C_0 (spiked concentration) measured in large reservoir with mass spectrometer
  - Valve measures C (breakthrough concentration) in the sampling reservoir every 10 minutes and C_0 every hour
- Diffusion measured on dry core and core saturated to 17%, 40%, 85% and 100% of total saturation

Experimental set up

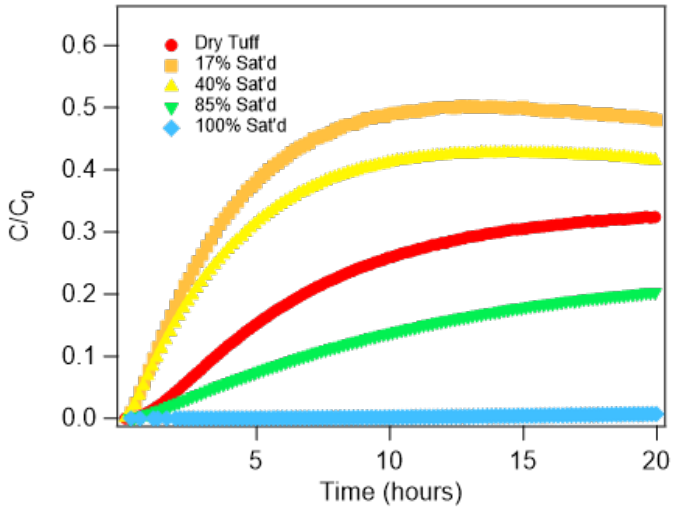


Core mineralogy (XRD)

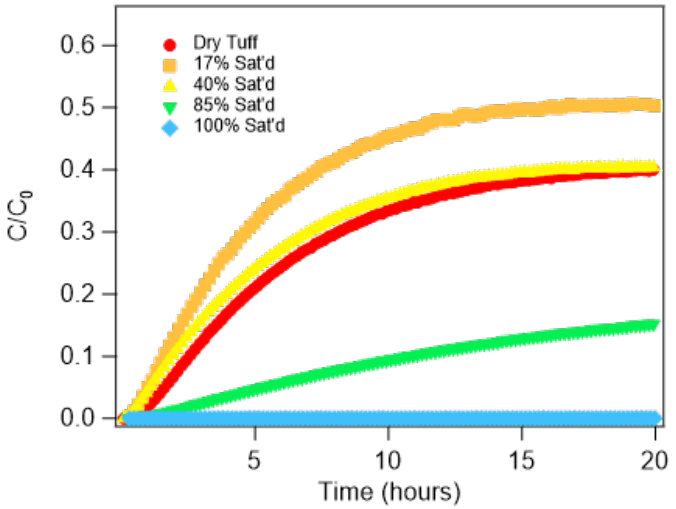


Fastest breakthrough in 17% saturated system

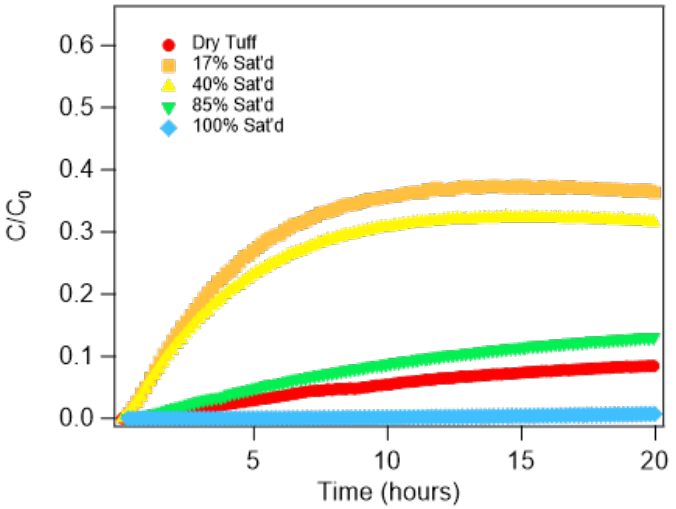
Krypton (Kr)



Sulfur hexafluoride (SF_6)



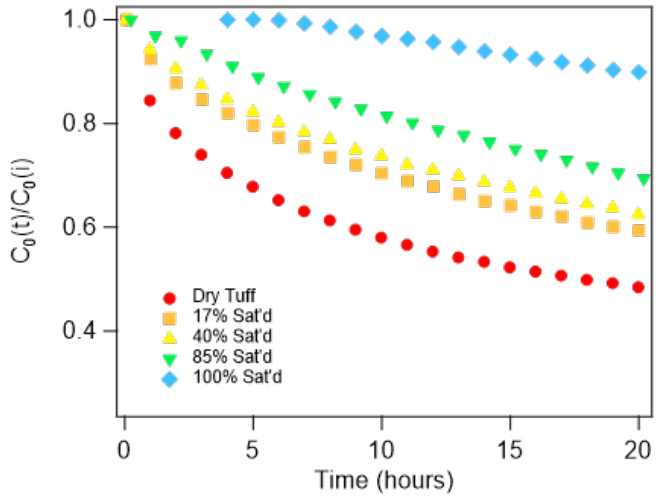
Xenon (Xe)



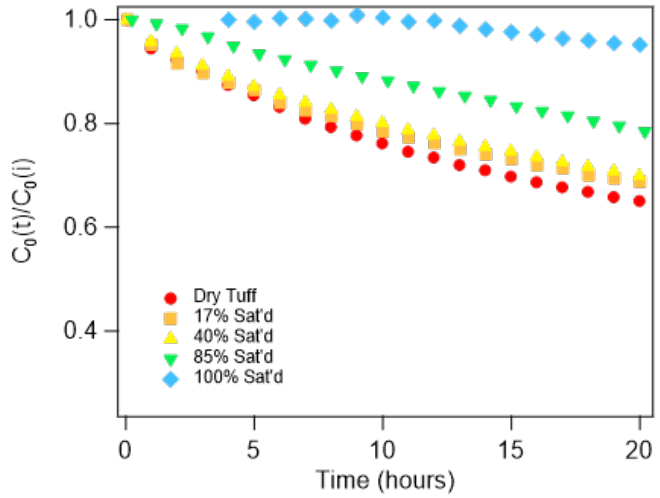
- Contrary to expectations of fast breakthrough in the dry core, diffusion was fastest in the 17% sat'd system for all gases
- The effects of higher saturations vary for all gases, with differing saturations above which diffusion slows to below that of the dry case
- **Significantly different Xe transport behavior**

Significant C_0 drop due to sorption by zeolites

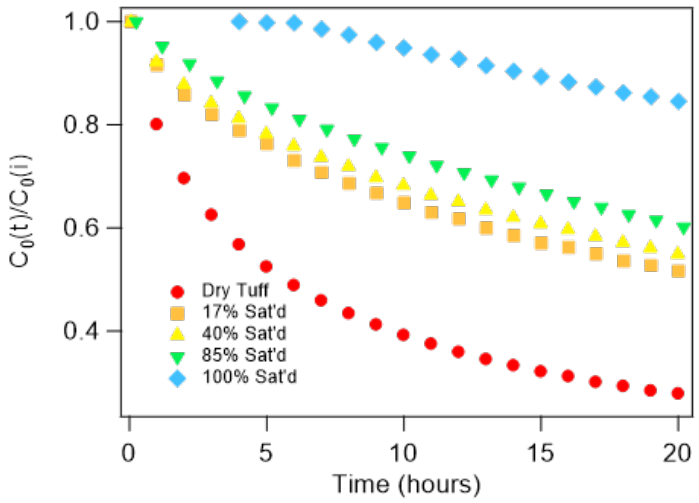
Krypton (Kr)



Sulfur hexafluoride (SF_6)



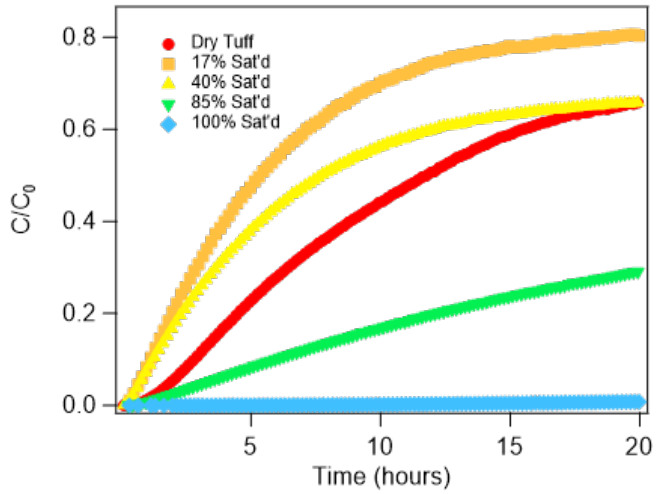
Xenon (Xe)



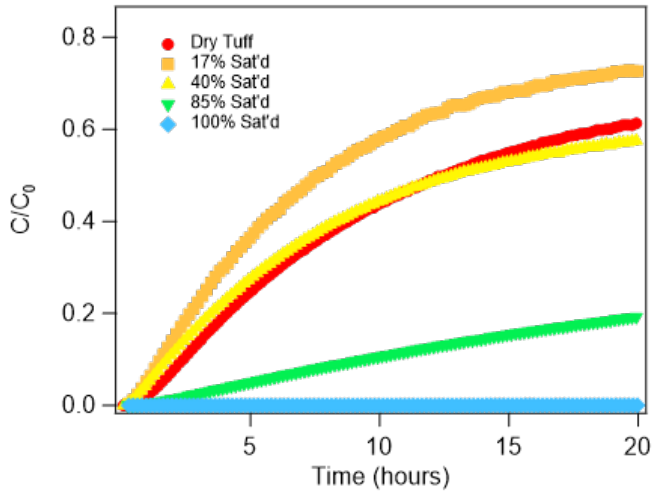
- Largest drop in C_0 in dry system for Xe, with large increase between dry and 17%
- **Significant sorption of tracer gases in the rock (Xe > Kr > SF_6)**
  - Explains why breakthrough is so slow, especially for Xe – sorption decreasing the driving force for diffusion

Normalization to $C_0(t)$ shows transport trends

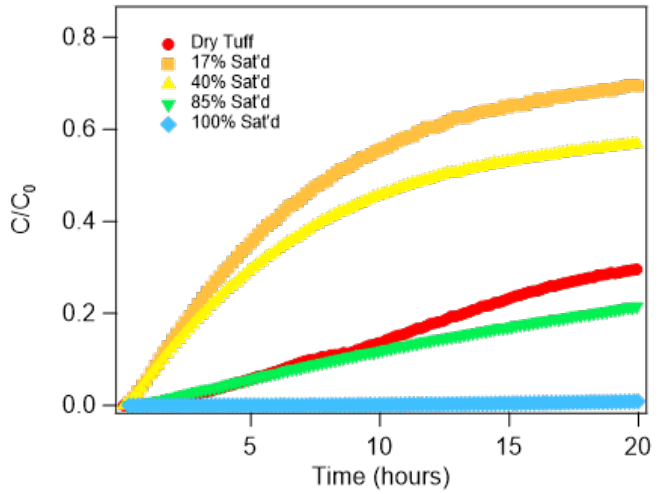
Krypton (Kr)



Sulfur hexafluoride (SF_6)



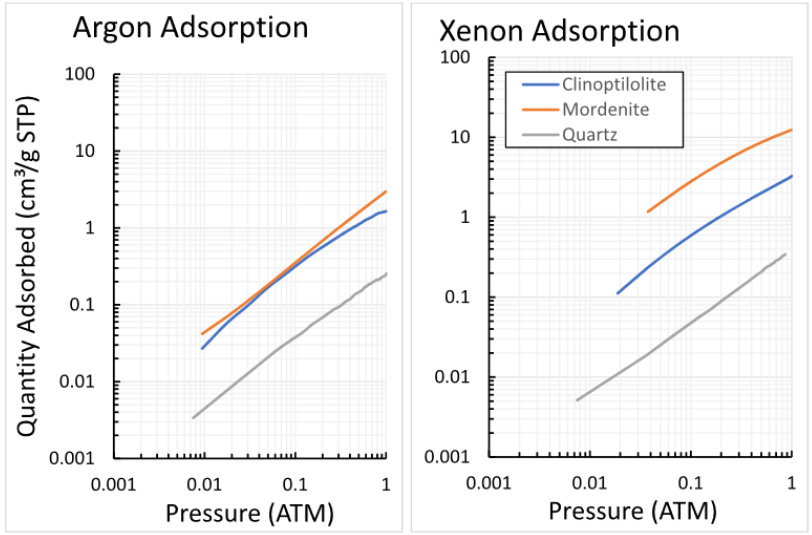
Xenon (Xe)



- For 17-100% sat'd systems, fastest breakthrough for Kr and very similar breakthroughs for SF_6 and Xe
  - In line with reported gas diffusion coefficients
- **Trends in dry case still show significant effects from sorption by zeolites**

Sorption by zeolites

- Recent publication by **Sandia National Lab** indicates that naturally-occurring, nanoporous zeolites will preferentially adsorb noble gases
- Effective porosity for both noble gases tested (Xe and Ar) exceeded one
  - 9.8 for Xe vs. 1.8 for Ar
- Results in fractionation of both arrival time and elemental concentrations relative to a source signal



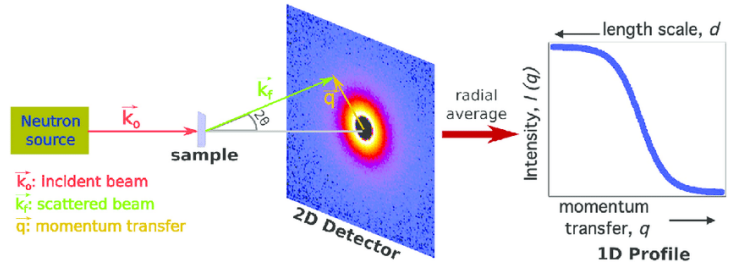
Isotherm adsorption measurements for argon and xenon

Feldman, J., et al., 2020. *Journal of Environmental Radioactivity*, *220*, p.106279.

Why is there such a significant change in gas uptake upon partial saturation with water?

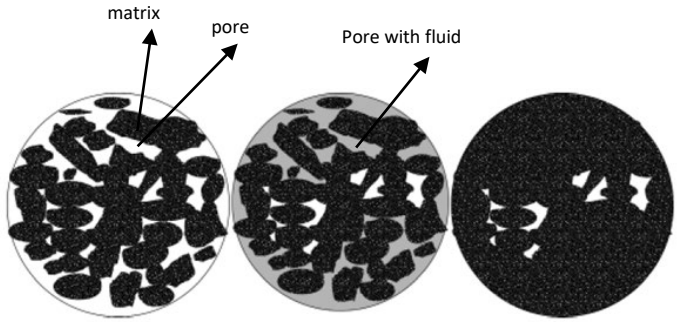
Investigating pore filling with SANS

- Small-angle neutron scattering (SANS) is a powerful technique capable of measuring changes in 1 to 100 nm pores.
- SANS measures the difference in scattering between a rock matrix and the pore space of a rock, i.e. the contrast.
  - Adding/removing fluid from nano-pores changes this contrast.
- During SANS experiments, rock powder was saturated incrementally with contrast-matched water to observe which pores fill as saturation increases



$$Q = \frac{4\pi}{\lambda} sin\theta \quad \lambda = 2dsin\theta \quad d = {}^{2\pi}/_{Q}$$

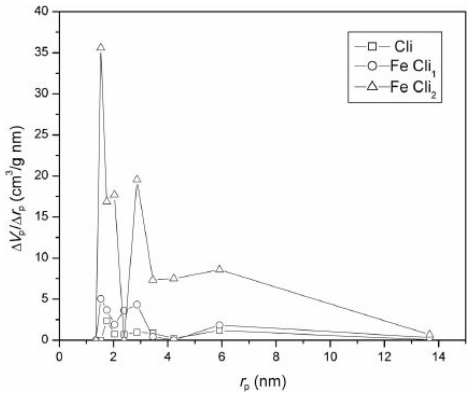
SANS technique



Contrast matching

Zeolite pores filled first with water

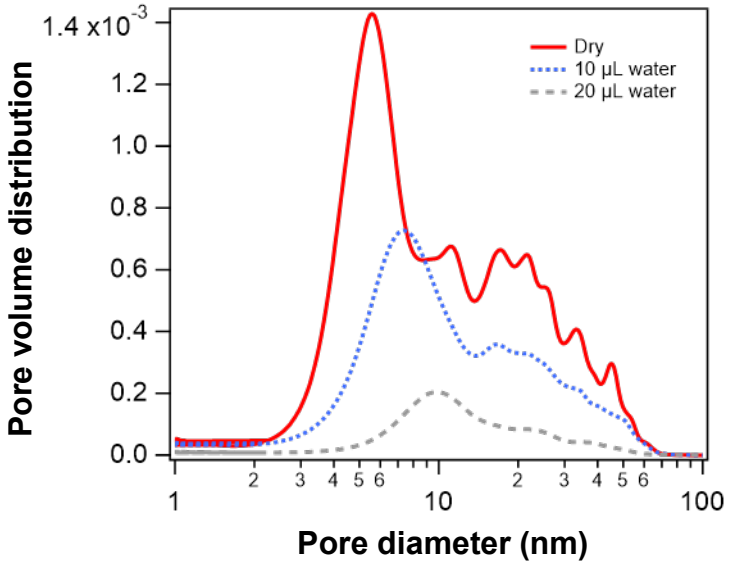
- Upon exposure to water, the initial filled nanopores were the smallest pores (~5.7 nm diameter)
- More water led to filling of most nanopores
- Previous studies found peak pore size of naturally-occurring zeolites to be between 2-4 nm radius



Zeolite pores are preferentially filled at low saturations, interfering with noble gas sorption.

Milićević, et al., 2013. *Clays and Clay Minerals*, *61*(6), pp.508-516.

Zeolitic Tuff Pore Filling



Conclusions and Ongoing work

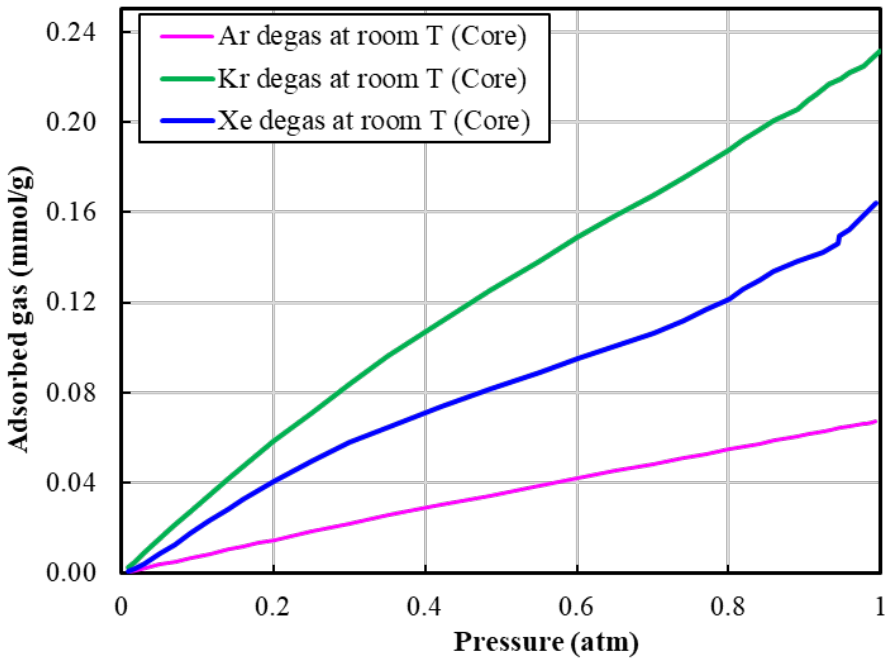
- Naturally-occurring zeolites greatly impact diffusive transport due to sorption
  - Will lead to retardation of signals and affect elemental fractionation due to different sorption preferences
- Low saturation will preferentially fill the small nanopores of zeolites, leading to less gas sorption
- Ongoing work includes:

1. Continued bench-scale studies of different rock types and relevant gases
2. **Collaboration with SNL:** Brunauer–Emmett–Teller (BET) surface area analysis of Kr, Xe, and SF_6 sorption
3. **Collaboration with EES-16:** Modeling with FEHM (Finite Element Heat and Mass) transfer code to calculate diffusion coefficients

Collaboration with SNL on gas sorption

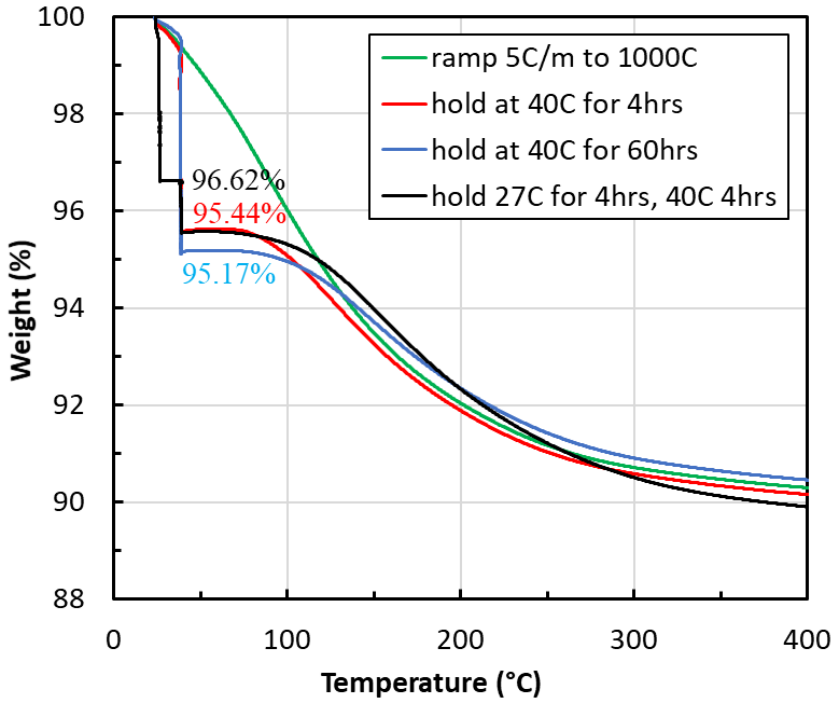
LYNM
LANL · LLNL · PNNL · SNL · NNSA

Collaborators: ***Guangping Xu, Scott Broome, Matt Paul & Jeffrey Greathouse***



Gas analyzer measurement

3.6% weight loss after initial 4 hrs degas and
1hr degas under vacuum before each measurement

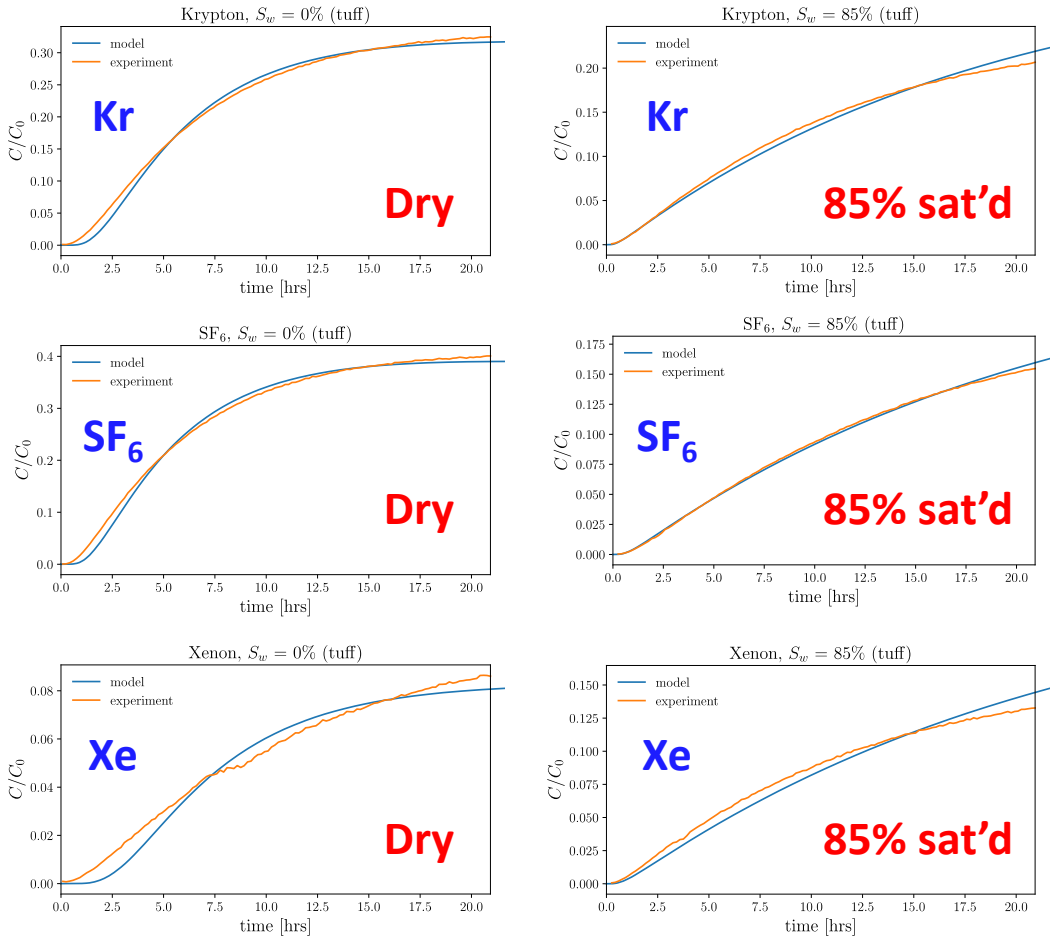


TGA measurement (under N_2 environment)

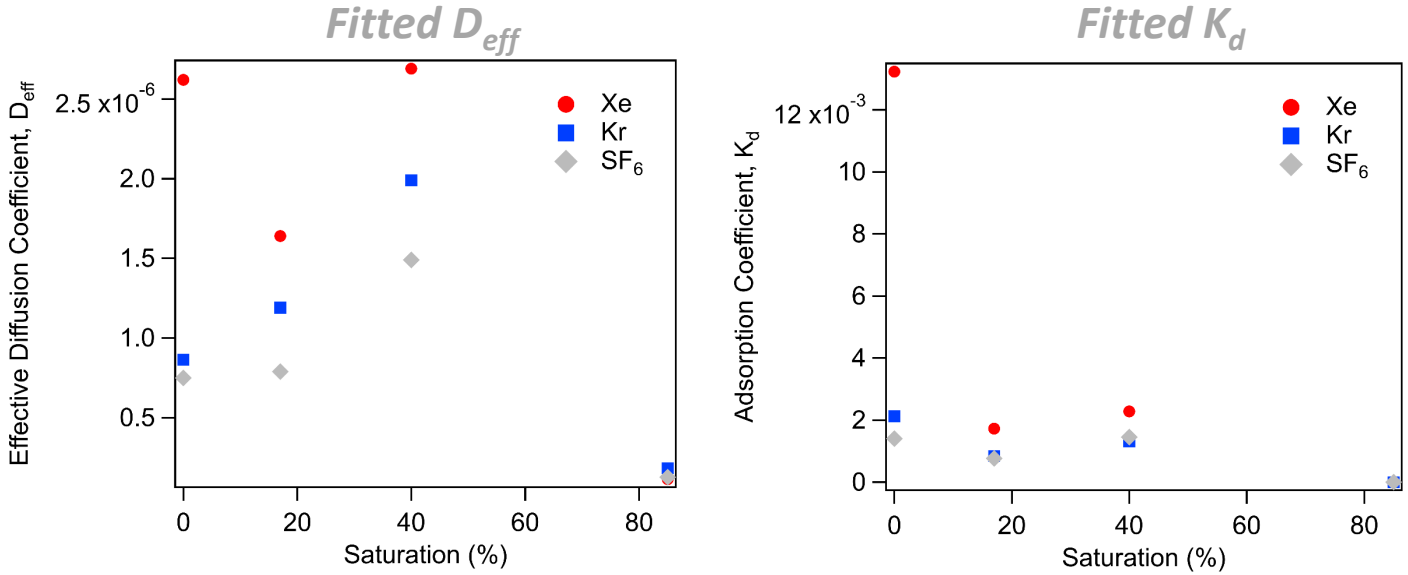
Water content	Core state
+ 5.5% H_2O	Fully saturated powder
+ 0% H_2O	Native (as received) state powder
- 3.4% H_2O	**Measurement state** (degas at room temperature under vacuum 4hrs)
- 4.8% H_2O	Dry powder (Baked at 40°C for 60 hours under N_2 environment)

- *Measurement state equivalent to **~14% saturation.***
- ***Fully saturated** with gas & at equilibrium*
- ***No competition** between gas species*

Collaboration with EES-16 on FEHM modeling



Collaborators: Phil Stauffer & John Ortiz



- Work in progress: **challenge to capture both breakthrough and spiked chamber behavior**
- Highest sorption for Xe dry, lowest diffusion for 85% sat'd system

Low Yield Nuclear Monitoring

Thank You!

Questions or comments?

Chelsea Neil

cwneil@lanl.gov

This research was funded by the National Nuclear Security Administration, Defense Nuclear Nonproliferation Research and Development (NNSA DNN R&D). The authors acknowledge important interdisciplinary collaboration with scientists and engineers from LANL, LLNL, MSTS, PNNL, and SNL.

Los Alamos NATIONAL LABORATORY EST. 1943 | Lawrence Livermore National Laboratory | Pacific Northwest NATIONAL LABORATORY | Sandia National Laboratories | NNSA National Nuclear Security Administration